

# SCIENCE FOR GLASS PRODUCTION

UDC 666.1.053.562(047).001.6

## A TECHNOLOGY FOR PRODUCING A NITROGEN-HYDROGEN PROTECTIVE ATMOSPHERE FROM NATURAL GAS

V. N. Bryzgalin,<sup>1</sup> V. I. Kondrashov,<sup>1</sup> and V. S. Bezlyudnaya<sup>1</sup>Translated from *Steklo i Keramika*, No. 1, pp. 5–6, January, 2002.

The authors consider the application in the glass industry of nitrogen-hydrogen protective atmospheres produced by different methods. The results of developing a technology of producing a protective atmosphere from natural gas are discussed.

The reliable protection of molten metal (tin) from oxidation and saturation with gases is essential in the production of high-quality sheet glass using the float method.

Thermodynamic calculations and practical experience show that in order to develop the necessary physicochemical conditions in a melting tank, the supplied nitrogen-hydrogen atmosphere should have a content of oxygen impurity not more than 0.0002 vol.% and a moisture content not more than 0.0010 vol.% (a dew point of  $-60^{\circ}\text{C}$ ).

The following three methods for producing a nitrogen-hydrogen atmosphere are used in the glass industry:

- mixing of separately obtained nitrogen produced by cryogenic air separation and electrolyzed hydrogen: used at the Borskii, Salavatskii, and Saratovskii (lines LDF-1 and LDF-2) Glass Works;

- direct combustion of ammonium with air at the Lisichanskii Glass Works (line LDF-2500);

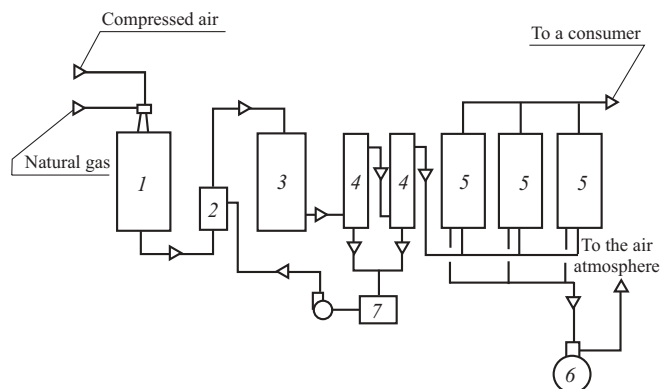
- incomplete high-temperature combustion of natural gas: Saratovskii Institute of Glass, the Kuvasaiskii and Gomelskii Works, and two-stream lines at the Saratovskii and Lisichanskii Works.

To meet the requirements imposed on the content of residual oxygen in a nitrogen-hydrogen atmosphere produced separately, a final purification stage based on a palladium catalyst is designed. Due to the high cost of the catalyst and the difficulties involved in maintaining a prescribed temperature regime, the final purification system virtually does not function; therefore, a protective atmosphere produced in accordance with this method has an increased content of oxygen.

The method for producing a nitrogen-hydrogen atmosphere by direct combustion of ammonia is simpler; how-

ever, the application area of this technology is limited due to difficulties involved in procuring a steady supply and safe storage of a required amount of liquid ammonium, which is the main initial material.

The simplest and most promising is the method for producing a nitrogen-hydrogen atmosphere from natural gas, which includes incomplete high-temperature combustion of natural gas, low-temperature steam conversion of carbon monoxide, and adsorption purification of the products of incomplete combustion from carbon dioxide and water vapor according to the scheme presented in Fig. 1. The advantages of this technology consist in the simplicity of the equipment,

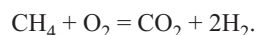
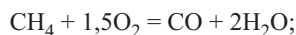
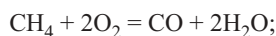


**Fig. 1.** Technological scheme of production of a protective atmosphere from natural gas: 1) incomplete combustion chamber for natural gas; 2) evaporator of condensate; 3) converter for catalytic purification from carbon monoxide; 4) water chillers; 5) adsorbers for purification from carbon dioxide and water vapor; 6) vacuum pump; 7) condenser system.

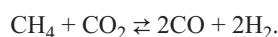
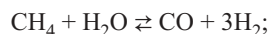
<sup>1</sup> Saratovskii Institute of Glass Joint-Stock Company, Saratov, Russia.

the possibility of full automation, a relatively small space needed, and significantly lower operating and capital costs.

Studies of the kinetics of the process of high-temperature air conversion of methane led to the assumption of a stepwise course of the process: in the first stage all available oxygen is consumed in the formation of carbon dioxide and water in accordance with the following levels of high-speed exothermic and generally irreversible reactions:



In the second stage the following endothermic reactions take place:



For a heterogeneous process (on fire grit), the sequence of chain reactions leads to the transformation of the  $\text{CH}_4 - \text{O}_2 - \text{CO}_2$  mixture into combustion products and then to the formation of CO and  $\text{H}_2$  and a subsequent reaction between  $\text{H}_2$  and  $\text{CO}_2$  that proceeds faster than the direct reaction.

A stepwise implementation of high-temperature conversion was planned in designing a combustion chamber (RF patent No. 1353725).

The volume of the chamber was filled with alternating layers of granular refractory materials with different specific surface areas (from the largest and to the smallest value) directed along the migration of the gas-air mixture, which made it possible to control the "volume" velocity in each layer via its height. Such filling of chambers makes it possible to initiate the conversion of methane at temperatures of 1500–1700°C (depending on the coefficient of the air flow rate) and end it at temperatures of 600–700°C.

The high temperatures facilitated the oxidation of methane at high velocities, and the uniform decrease in the temperature facilitated the reactions of hydrogenation. Such implementation of the high-temperature conversion of natural gas in the combustion chamber yielded a gas mixture in which the residual oxygen content did not exceed 0.0001–0.0002 vol. %.

The next stage of this process is the low-temperature steam conversion of carbon monoxide based on copper-zinc catalysts.

The final stage of the production of a protective atmosphere is its adsorption purification from carbon dioxide and water vapor. The purification is conducted in a stationary layer of synthesized zeolite NaX. Its regeneration principle consists in developing kinetic conditions for the separation of adsorbed  $\text{CO}_2$  and  $\text{H}_2\text{O}$  from the pores and removing them from the layer.

The use of zeolite for adsorption purification of a protective atmosphere from  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in a cyclic process with regeneration of the pressure difference is determined by the substantial dipole moment of the molecules of  $\text{H}_2\text{O}$  and the quadrupole moment of the  $\text{CO}_2$  molecules, which increases the electrostatic component of adsorption interaction, thus reaching 90% for  $\text{H}_2\text{O}$  and 50% for  $\text{CO}_2$ .

All these specifics provide for high selectivity of adsorption of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  molecules.

A review of the existing methods for purification of a protective atmosphere from  $\text{H}_2\text{O}$  and  $\text{CO}_2$  revealed that the most effective method is a short-cycle adsorption with regeneration of zeolite using reverse blowing with a pure gas under a low residual pressure developed by evacuation.

The desorption half-cycle is crucial in the cyclic process of adsorption purification of a protective atmosphere. The fullness of desorption of zeolite determines the reversibility of the process, the purity of the protective atmosphere generated, and the efficiency of the adsorption plant. On the other hand, correct choice of the desorption parameters makes it possible to reach the required degree of purification of the protective atmosphere with minimum consumption of energy.

The pressure difference between the adsorption and the desorption half-cycles is generated by vacuum treatment of the zeolite layer with a decreasing pressure during the desorption half-cycle. A decrease in the pressure correlates with an increasing linear velocity of the gas during the desorption half-cycle, and a concentration gradient is continuously developed between the adsorbate and the adsorbent in the entire active zone of the zeolite layer. Consequently, the removal of the adsorbates in the desorption half-cycle is implemented in two ways: via diffusion into the gas medium along the entire layer with subsequent removal of the gas flow and via migration of the sorption fronts towards the flow of the blowing gas.

Due to the higher partial pressure of  $\text{CO}_2$  in the initial protective gas and its less perceptible nonlinearity of isotherms, a substantial part of  $\text{CO}_2$  is simultaneously removed at the initial moment of the desorption half-cycle from the whole active zone.

It should be noted that the presence of drop moisture in the front layer of zeolite decreases its effect and may result in irreversible modifications of the crystalline structure of zeolite and in its mechanical destruction. The water steam concentration at a temperature of 30°C is 30 g/m<sup>3</sup>.

To prevent the negative effect of drop moisture on the process of adsorption purification of a protective atmosphere, the moisture content should not exceed 2–3%, or 0.6–1.0 g/m<sup>3</sup>. This is achieved through the use of dehumidifiers installed in the adsorbers at the entrance to the adsorbent layer.

Based on the performed studies, the Saratov Institute of Glass has developed a nitrogen-hydrogen plant (AVU-400) with a capacity of 400 m<sup>3</sup>/h of a purified protective atmosphere.

The volume content of impurities in the protective atmosphere obtained according to the developed technology does not exceed 0.0002% for oxygen, 0.0010% (dew point – 60°C) for moisture, and 0.0050% for carboniferous impurities.

The use of the developed technology for producing a protective atmosphere from natural gas makes it possible to lower its production cost with respect to the main param-

eters, as compared to other methods used in the glass industry. The cost of production of a protective atmosphere for float glass decreased more than 2.5 times. New technical solutions have been developed in the last 3 – 4 years, making it possible to further diminish the cost of production of the protective atmosphere.